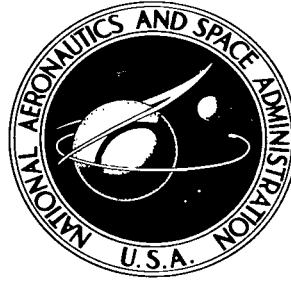


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TRANSPORT PROPERTIES OF DILUTE GAS MIXTURES

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SUMMARY

Experimental diffusion coefficients, mixture viscosities, and mixture thermal conductivities for the binary systems helium-argon, helium-hydrogen, hydrogen-nitrogen, argon-ammonia, and hydrogen-ammonia have been analyzed to obtain insight as to the concordance between theory and experiment. The analysis suggested the following conclusions: (1) the diffusion coefficients and viscosities of gas mixtures of polyatomic and polar species are well described by the Chapman-Enskog theory, (2) the Chapman-Enskog theory for the thermal conductivity of monatomic gas mixtures seems to be valid, (3) approximate methods that take account of the contribution of the internal energy flux in mixtures involving polyatomic and polar gases seem promising, and (4) only new experimental data of high accuracy and precision will further testing and understanding of theory. The greatest need is for thermal conductivity data.

INTRODUCTION

There is a wealth of experimental data on the transport properties of gas mixtures, diffusion coefficients, mixture viscosities, and thermal conductivities, as well as results on thermal diffusion. Rather than attempting some sort of statistical assessment of all this information, a few simple systems that typify interactions among various types of molecules - monatomic and polyatomic, nonpolar and polar - are examined in the hope of obtaining some insight as to the concordance between theory (rigorous or approximate) and experiment (painstaking or perfunctory).

To this end, five binary gas systems are considered near room temperature, since precise data are most easily obtained here. For the systems chosen, there are data on the three most important transport properties: binary diffusion coefficient, mixture viscosity, and mixture thermal conductivity. Thermal diffusion data are also available for some of these mixtures, but no analysis or detailed consideration is given here.

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Systems have been selected to avoid undue complexity; ternary or multi-component mixtures are not examined, since the behavior of these systems should be understandable in terms of the behavior of binary systems. Similarly, systems involving interacting pairs of complex polyatomic (and possibly polar) molecules have been avoided.

In general, it is expected that the rigorous Chapman-Enskog theory for monatomic gases should serve rather well in describing the diffusivity and viscous properties of polyatomic gases. In the case of the thermal conductivity, however, a diffusive flux of internal energy (rotation, vibration, etc.) can make a substantial contribution to the heat flux and must be considered. To this end, the recent approximate theory of Mason and Monchick (ref. 1) for the heat conductivity of polyatomic and polar gases is invoked and extended (in an approximate fashion) to gas mixtures. Specifically, the following mixtures have been examined.

(1) Helium-argon. Since this is a mixture of monatomic gases that obey a spherically symmetric intermolecular force law, the rigorous Chapman-Enskog treatment is expected to be fully applicable.

(2) Helium-hydrogen. This is a mixture of a monatomic gas with a diatomic molecule whose only internal energy is rotational. The transfer of energy between translation and rotation is slow for hydrogen and requires several hundred collisions. Thus, it should be possible to treat the transport of translational and internal energies separately.

(3) Hydrogen-nitrogen. This is a mixture of diatomic gases that possess rotational internal energy only. In examining the thermal conductivity, however, the translation-rotation relaxation in nitrogen must be considered.

(4) Argon-ammonia. This mixture involves the interaction of a monatomic gas with a gas possessing an appreciable dipole moment.

(5) Hydrogen-ammonia. This mixture involves a polar molecule and a diatomic molecule.

In general, the emphasis here is on mixture properties; hence, the formulas are adjusted to give perfect predictions as to the properties of the pure components. To this end, experimental thermal conductivities were corrected to be in accord with theory for the pure gases for those substances where the theory seems sound and nearly rigorous - helium, argon, and hydrogen. Experimental conductivities of nitrogen and ammonia have been assumed correct, and a rotational relaxation time has been assigned to make the experimental thermal conductivity of nitrogen or ammonia correspond to the theory of Mason and Monchick (ref. 1).

THEORETICAL CONSIDERATIONS

In general, the transport properties of dilute gas mixtures involve terms characteristic of the interaction of the pure components with themselves and also all possible pairwise interactions between unlike species. The self-

interactions give rise to the properties of the pure species - not the subject of this report.

Diffusion Coefficient

The parameter that most directly characterizes the unlike interactions is the diffusion coefficient. Data have been analyzed in terms of the first Chapman-Enskog approximation (ref. 2, eq. 8.2 - 44) in most cases corrected by an average of the Kihara second approximations (ref. 3) calculated for the extremes of composition.

Mixture Viscosity

An analysis of mixture viscosity has been made in terms of the first Chapman-Enskog approximation (ref. 2, eqs. 8.2 - 22). In most cases, however, the quantity η_{12} (ref. 2, eqs. 8.2 - 21), derived from diffusion has been corrected according to the third Chapman-Enskog approximation for pure gases.

Mixture Thermal Conductivity

For monatomic gas mixtures, mixture thermal conductivities have been obtained from the expression of reference 4. This expression was also used to compute the translational energy contribution to the conductivity for the other mixtures, but with an appropriate correction, as discussed subsequently. The internal energy for mixtures has been computed according to Hirschfelder's Eucken type approximation for mixtures (ref. 5), again with an appropriate correction. The use of the equation of reference 4 for the translational thermal conductivity with Hirschfelder's equation for the internal thermal conductivity is justified if it is assumed that inelastic collisions are rare. This assumption is necessary in order that the translational distribution function should not be unduly perturbed, so that the translational conductivity is related to the viscosity or diffusion coefficients as in the case of the noble gases. It seems that this assumption is justified except in the case of rotation-translation interchange, which occurs every few collisions (i.e., 2 to 20).

Approximate expressions have been derived for the thermal conductivity of pure polyatomic gases taking account of inelastic collisions (ref. 1). It has been shown that the translational conductivity is less than that of a monatomic gas:

$$\lambda_{\text{trans}} = \lambda_{\text{mon}} \left[1 - \frac{2}{\pi} \left(\frac{5}{2} - \rho \frac{D}{\eta} \right) \frac{C_{\text{rot}}}{C_{v,\text{trans}}} \frac{1}{Z} \right] \quad (1)$$

where C_{rot} and $C_{v,\text{trans}}$ are the rotational and translational portions of the heat capacity, while Z is the collision number for rotational relaxation.

On the other hand, the internal energy contribution to the conductivity is enhanced:

$$\lambda_{\text{int}} = \lambda_{\text{int,ME}} \left[1 + \frac{2}{\pi} \left(\frac{5}{2} - \rho \frac{D}{\eta} \right) \frac{C_{\text{rot}}}{C_{\text{int}}} \frac{1}{Z} \right] \quad (2)$$

where $\lambda_{\text{int,ME}}$ is the modified Eucken expression for the internal thermal conductivity. As yet, no comparable theory for mixtures has been published. Consequently an extension to binary mixtures is used, which is arrived at intuitively as follows: Assume that the mixture conductivity may be written

$$\lambda_{\text{mix}} = \lambda_{\text{mix,ME}} + \Delta\lambda_1 + \Delta\lambda_2 \quad (3)$$

where $\Delta\lambda_1$ and $\Delta\lambda_2$ are the deviations attributable to the separate components. An approximate formula (ref. 6) for the conductivity of a monatomic gas mixture is

$$\lambda_{\text{mix,mon}} \cong \frac{\lambda_{1,\text{mon}}}{1 + \psi_{12} \frac{x_2}{x_1}} + \frac{\lambda_{2,\text{mon}}}{1 + \psi_{21} \frac{x_1}{x_2}} \quad (4)$$

where $\lambda_{1,\text{mon}}$ and $\lambda_{2,\text{mon}}$ are the conductivities of the pure components, x_1 and x_2 are mole fractions, and ψ_{12} and ψ_{21} are functions of the molecular weights and cross sections (ref. 6). Hirschfelder's formula for the internal thermal conductivity is of the same form as equation (4), but with $\lambda_{\text{int,ME}}$ in place of the λ_{mon} , and ψ_{ij} replaced by D_i/D_{ij} (D_i is the self-diffusion coefficient, and D_{ij} is the binary diffusion coefficient between components i and j).

It is assumed here that, in a mixture, the terms Z_i^{-1} may be replaced by

$$Z_{i,\text{mix}}^{-1} = x_i Z_i^{-1} + x_j Z_{ij}^{-1} \quad (5)$$

Hence, from equations (1), (2), (4), (5), and Hirschfelder's internal conductivity formula, it can be inferred that

$$\Delta\lambda_1 = \frac{2}{\pi} \left(\frac{5}{2} - \rho \frac{D}{\eta} \right)_1 C_{1,\text{rot}} \left(\frac{x_1}{Z_1} + \frac{x_2}{Z_{12}} \right) \times \left(\frac{\frac{\lambda_{1,\text{int,ME}}}{C_{1,\text{int}}}}{1 + \frac{D_1}{D_{12}} \frac{x_2}{x_1}} - \frac{\frac{\lambda_{1,\text{mon}}}{C_{1,\text{trans}}}}{1 + \psi_{12} \frac{x_2}{x_1}} \right) \quad (6)$$

The formula for $\Delta\lambda_2$ is obtained from equation (6) by interchanging subscripts 1 and 2. Thus, equations (3) and (6) were used in analyzing data on mixtures involving nitrogen and ammonia.

As mentioned in the INTRODUCTION, mixture conductivities were corrected so as to match theoretical values for helium, argon, and hydrogen. Hot-wire thermal-conductivity cells measure, in essence, the reciprocal of the conductivity. Thus, if λ_1^* and λ_2^* are the experimentally reported conductivities of the pure components and λ_{mix}^* is the experimental mixture value, while

λ_1 and λ_2 are the theoretical conductivities of the pure components, the corrected mixture conductivity λ_{mix} is

$$\lambda_{\text{mix}}^{-1} = \left(\lambda_{\text{mix}}^{*-1} - \lambda_1^{*-1} \right) \frac{\lambda_2^{-1} - \lambda_1^{-1}}{\lambda_2^{*-1} - \lambda_1^{*-1}} + \lambda_1^{-1} \quad (7)$$

RESULTS AND DISCUSSION

Helium-Argon System

Diffusion coefficients for the helium-argon system were calculated by assuming the exponential-6 potential with the force constants $r_m = 3.505$ angstroms $\alpha = 13.21$, and $\epsilon/k = 33.4^\circ \text{K}$. The values for α and ϵ/k are taken from reference 3, while r_m was adjusted to fit the experimental data of reference 7 at 25°C and 1 atmosphere. Comparison between theory and experiment are shown in the following table:

Helium mole fraction	Diffusion coefficient, cm^2/sec		Ratio of second Kihara approximation to first Chapman-Enskog approximation, $f_D^{(2)}$
	Experimental	Calculated	
0.0 (trace helium)	0.754	0.750	1.0284
1.0 (trace argon)	.725	.729	1.0001

The factor $f_D^{(2)}$ is the ratio of the second Kihara approximation to the first Chapman-Enskog approximation. Of course, the agreement between experiment and theory is not surprising, since r_m was chosen to obtain a good fit. The experimentally observed variation of diffusion coefficient with concentration is somewhat larger than that pre-

dicted theoretically, but it is not clear if this is a real effect or merely experimental error.

Viscosities for helium-argon mixtures were calculated again by assuming the exponential-6 potential with force constants as follows:

Mixture	Exponential-6 force constants		
	$r_m, \text{\AA}$	α	$\epsilon/k, ^\circ\text{K}$
Helium-helium	3.109	12.4	9.16
Argon-argon	3.858	14.0	123.2
Helium-argon (combining rules)	3.471	13.21	33.4
Helium-argon (diffusion)	3.494	13.21	33.4

Again the force constants α and ϵ/k are from reference 3; for pure helium and argon, r_m has been chosen to fit the recent, precise viscosity determinations of reference 8. Two values of r_m for the unlike interaction have been tested - the first from the empirical combining rules of reference 3, and the second obtained from the experimental diffusion coefficients as follows:

$$r_{m,vis}^2 = \frac{r_{m,dif}^2}{f_{\eta}^{(3)}} \quad (8)$$

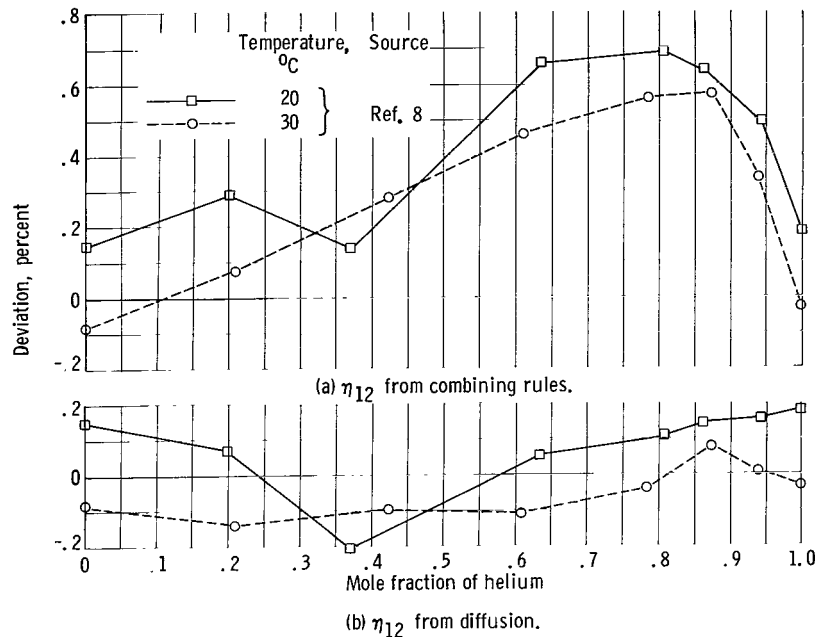


Figure 1. - Deviation of theoretical from experimental viscosities for helium-argon mixtures.

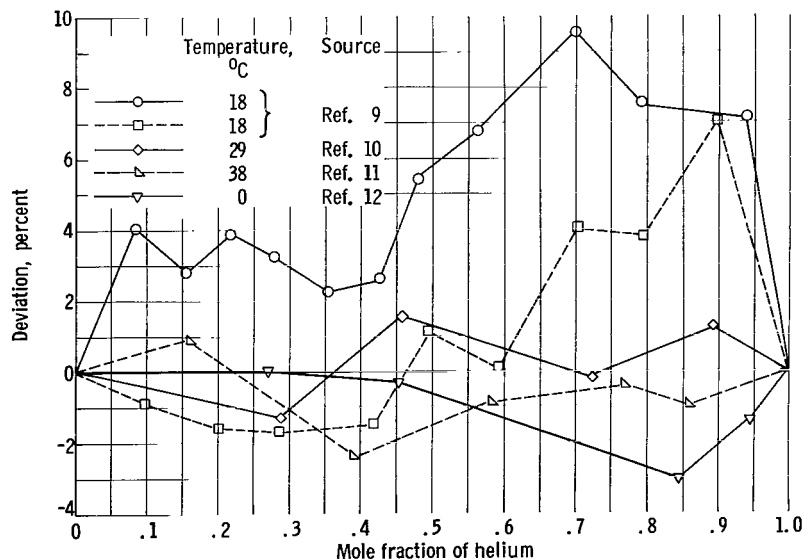


Figure 2. - Deviation of experimental from theoretical thermal conductivities for helium-argon mixtures. λ_{12} from diffusion.

where $f_{\eta}^{(3)}$ is the correction for the third approximation for the viscosity of a pure gas (in this case, 1.0062). This procedure lacks elegance but is probably a correction in the right direction. Theory and experiment are compared in figure 1. Although the calculations based on the combining rule are fair - the worst deviation being only 0.7 percent - the force constants derived from diffusion are clearly to be preferred. Thus, the agreement between the diffusion and viscosity data is encouraging and seems to confirm fully the rigorous Chapman-Enskog theory. In fact, the viscosity data are apparently of a quality that justifies a proper calculation of the second approximation.

Thermal conductivities have been computed by using the force constants ($r_m = 3.494 \text{ \AA}$ for the He-Ar interaction); deviations of experiment (refs. 9 to 12) from theory are shown in figure 2. Clearly the deviations are much more serious, amounting to 1.5 percent in the best case (ref. 10), with errors approaching 10 percent at worst (ref. 9). In an overall

sense, the errors seem random rather than systematic, and there seems no cause for questioning the rigorous theory. The computed conductivities are perhaps more reliable than the experimental values for this system.

Data on thermal diffusion in helium-argon mixtures has been analyzed in reference 4; agreement between theory and experiment seems satisfactory.

Helium-Hydrogen System

Diffusion coefficients have been measured in reference 13 with what appears to be good precision and accuracy. Here they have been calculated by

Range of helium mole fraction	Diffusion coefficient, cm ² /sec		Ratio of second Kihara approximation to first Chapman-Enskog approximation $f_D^{(2)}$
	Experimental	Calculated	
0 (trace helium)	-----	1.544	1.0021
0 to 1.00	1.549	-----	-----
0.1490 to 1.000	1.550	-----	-----
0.4537 to 1.000	1.572	-----	-----
1.00 (trace hydrogen)	-----	1.561	1.0131

assuming the exponential-6 potential with force constants $r_m = 3.289$ angstroms, $\alpha = 13.22$, and $\epsilon/k = 18.27^\circ \text{K}$ (α and ϵ/k from ref. 3), with r_m adjusted to bracket the data of reference 13 at 25°C and 1 atmosphere shown at the left. Again, the experimental variation of diffusion coefficient with composition seems somewhat larger than the theoretical, but, in this case, the experimental

compositions embrace a range of values, so that the comparison is less meaningful.

Viscosities and thermal conductivities for helium-hydrogen were calculated by assuming force constants as follows:

Mixture	Exponential-6 force constants		
	$r_m, \text{\AA}$	α	$\epsilon/k, ^\circ \text{K}$
Helium-helium	3.100	12.4	9.16
Hydrogen-hydrogen	3.337	14.0	37.3
Helium-hydrogen (combining rules)	3.226	13.22	18.27
Helium-hydrogen (diffusion)	3.278	13.22	18.27

The force constants α and ϵ/k are again from reference 3, with r_m for the pure components adjusted to reproduce reasonably the experimental data (refs. 14 and 15) for these gases, and r_m for the helium-hydrogen interaction adjusted according to equation (8) for $f_\eta^{(3)} = 1.0063$. Theoretical viscosity calculations are compared with experiment in figure 3.

Once more, the agreement between the diffusion and viscosity data is encouraging. (It should be noted, however, that the viscosities seem considerably less precise than those for the helium-argon mixtures, with deviations of 1 to 2 percent rather than 0.2 percent.) Thermal conductivities computed according to the modified Eucken approximation for mixtures are compared with the experimental results of reference 16 in figure 4. (The modified Eucken approximation assumes that the collision numbers Z_{H_2} and $Z_{\text{H}_2\text{-He}}$ are sufficiently large so that the correction of equation (6) is negligible.) Clearly, these data seem

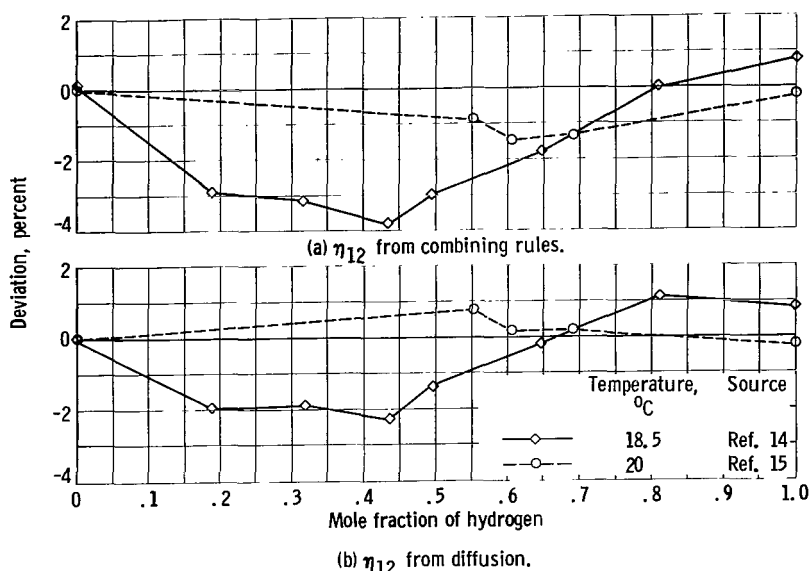


Figure 3. - Deviation of experimental from theoretical viscosities for hydrogen-helium mixtures.

helium-hydrogen mixtures (ref. 17). From this fact alone, one can establish a maximum slope to the conductivity-concentration plot at zero hydrogen concentration. Further, the data of reference 18 indicate that a mixture containing 17.3 percent hydrogen has the same thermal conductivity as pure helium; the consequences of this fact are indicated as a solid symbol in figure 4.

In summary, it seems that the rigorous Chapman-Enskog theory properly represents the relation between diffusion coefficients and viscosities of helium-argon mixtures. It is not clear whether the modified Eucken approximation describes the thermal conductivities of these mixtures. Experimental data of enhanced accuracy are clearly required. Thermal diffusion data have been analyzed in reference 2 (p. 584).

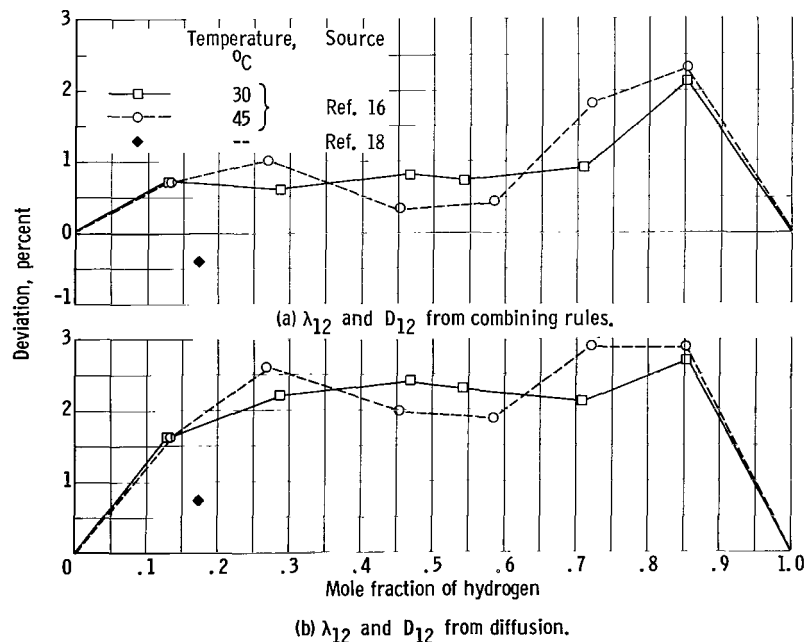


Figure 4. - Deviation of experimental from theoretical thermal conductivities for hydrogen-helium mixtures.

to favor the force constants from the empirical combining rules over unlike interaction force constants determined from diffusion coefficients or mixture viscosities. (It might be noted that these experimental data are in even closer accord with the theoretical analysis accompanying the data.)

However, from research on thermal-conductivity detectors used for gas chromatography it is well known that small amounts of hydrogen decrease the thermal conductivity of

Experimental data of enhanced accuracy are clearly required. Thermal diffusion data have been analyzed in reference 2 (p. 584).

Hydrogen-Nitrogen System

Diffusion coefficients have been measured by using a Loschmidt type cell (ref. 13); no information was obtained on concentration dependence. Values have been calculated with the assumption of $r_m = 3.686$ angstroms (to fit the experiment),

$\alpha = 15.56$ and $\epsilon/k = 58.97^\circ \text{K}$ (calculated according to ref. 3). Comparison of hydrogen-nitrogen diffusion coefficients at 1 atmosphere are shown in the following table:

Hydrogen-nitrogen diffusion coefficients, cm^2/sec			
Temperature, $^\circ\text{C}$	Hydrogen mole fraction		
	0 (a)	0 to 1 (b)	1 (a)
25	0.7842	0.7835	0.7598
55	.9232	.9079	.8944
85	1.071	1.052	1.037
$f_D^{(2)}(55)$	1.03220	-----	1.00006

^aCalculated.

^bExperimental.

The correction for the second approximation was calculated at 55°C and then applied at the other temperatures as well; however, this factor varies only very slightly with temperature.

Viscosities and thermal conductivities for hydrogen-nitrogen mixtures were calculated from the force constants in the following table. All values were taken from reference 3 except for r_m from diffusion, again adjusted according to equation (8) with $f^{(3)} = 1.0063$. In figure 5(a), η

experimental viscosities from references 14 and 19 are compared with theoretical values calculated by using $r_{m, \text{H}_2-\text{N}_2}$ from diffusion. (Values from combining rules were only slightly different and hence are not shown.) The agreement between viscosity and diffusion data again seems satisfactory.

Mixture	Exponential-6 force constants		
	$r_m, \text{\AA}$	α	$\epsilon/k, ^\circ\text{K}$
Hydrogen-hydrogen	3.337	14.0	37.3
Nitrogen-nitrogen	4.011	17.0	101.2
Hydrogen-nitrogen (combining rules)	3.690	15.56	58.97
Hydrogen-nitrogen (diffusion)	3.675	15.56	58.97

Thermal conductivities have been computed from equations (3) and (6) with $Z_{\text{H}_2} = Z_{\text{H}_2-\text{N}_2} = \infty$ and $Z_{\text{N}_2} = Z_{\text{N}_2-\text{H}_2} = 7.2$. Theory and experiment (ref. 20) are compared in figure 5(b). Also shown, as a dash-dot curve is the modified Eucken type approximation corresponding to $Z_{\text{N}_2} = Z_{\text{N}_2-\text{H}_2} = \infty$. It would seem that the apparent discord between theory and

experiment cannot be rationalized by the choice of larger collision numbers. Once again better experimental conductivity data would be most welcome.

Argon-Ammonia System

Diffusion coefficients for this system have recently been determined (ref. 21). In reference 21 experimental data were fitted to the Lennard-Jones 12-6 potential with $\sigma = 3.286$ angstroms and $\epsilon/k = 224.65^\circ \text{K}$. These values agree quite closely with estimates based on empirical combining rules for viscosity force constants of the pure components ($\sigma = 3.271 \text{\AA}$ and $\epsilon/k = 221^\circ \text{K}$). Viscosities of argon-ammonia mixtures have also been measured (ref. 22). These data are analyzed here by choosing viscosities of pure

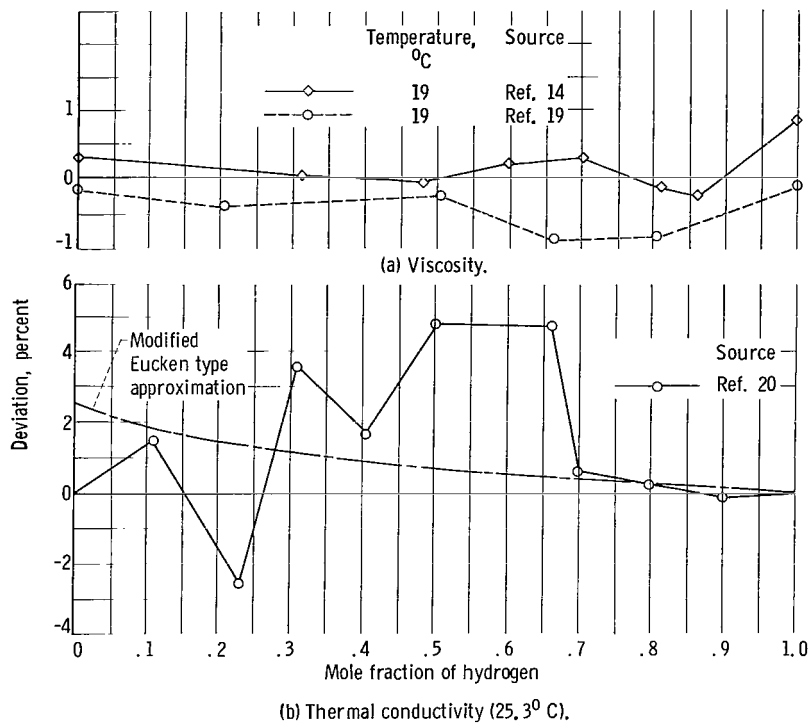


Figure 5. - Deviation of experimental from theoretical viscosities and thermal conductivities for hydrogen-nitrogen mixtures (η_{12} , D_{12} , λ_{12} from diffusion).

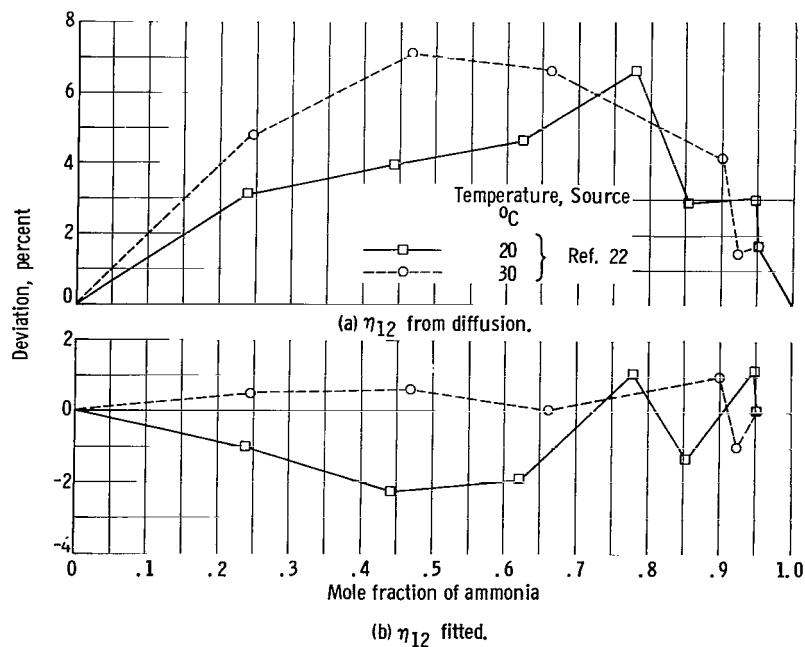


Figure 6. - Deviation of experimental from theoretical viscosities for ammonia-argon mixtures.

ammonia and argon and calculating the parameters characterizing the unlike interaction from the force constants derived from diffusion; the results are shown in figure 6. Clearly, there is a serious discrepancy, with experimental viscosities as much as 7 percent larger than theory. It is possible to obtain agreement by arbitrarily taking $\sigma = 3.072$ angstroms for the unlike interaction. This is equivalent to assuming that the measured diffusion coefficients are too low (by 14.4 percent). Figure 6(b) shows that accord between theory and experiment is much improved; errors are generally in the range of 1 to 2 percent. (It might be noted that these experimental data appear much less precise than the results for the helium-argon system in ref. 8.)

In the hope of resolving the serious discrepancy between the viscosity and diffusivity data, thermal conductivities of these mixtures at 300° K were measured. A hot-wire thermal-conductivity apparatus was used and calibrated with helium and argon. The conductivities of these gases were assumed to be 370.9 and 42.42 microcalories per centimeter per second per °K,

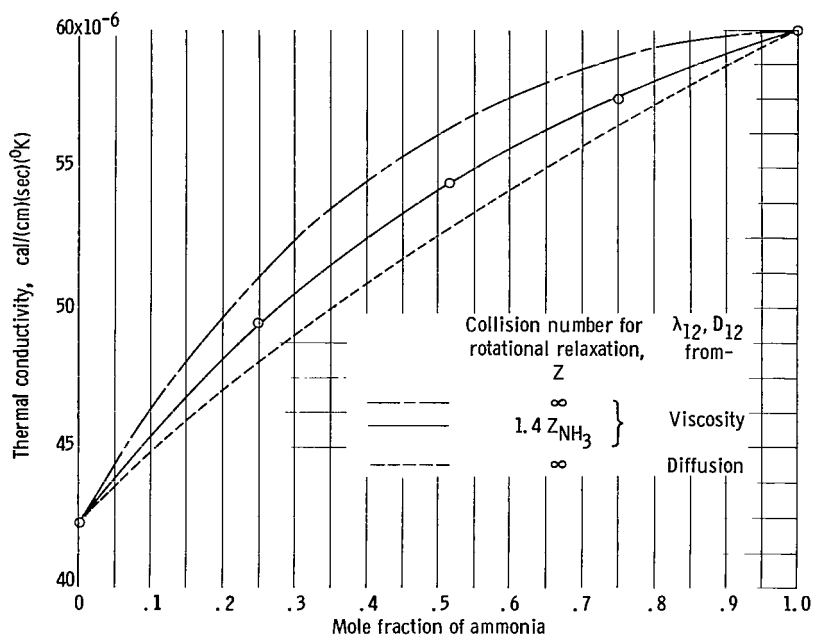


Figure 7. - Thermal conductivity of ammonia-argon mixtures (300° K).

the experimental conductivities are compatible with the viscosity results but incompatible with the diffusion coefficients. As a matter of fact, by assuming $Z_{\text{NH}_3\text{-Ar}} = 1.4 Z_{\text{NH}_3}$, the experimental data can be fitted almost perfectly. Thus, the experimental diffusion coefficients (ref. 21) for the ammonia-argon system are clearly suspect and should be remeasured.

Hydrogen-Ammonia System

Diffusion coefficients for this system have been measured (ref. 13); the results were fit by assuming a

Lennard-Jones 12-6 potential with $\sigma = 2.933$ angstroms and $\epsilon/k = 142.7^\circ \text{ K}$. (The value of ϵ/k was obtained in ref. 13 from a fit of the first Chapman-Enskog approximation to the data over a range of temperature; σ has been deduced by applying an average correction for the second Kihara approximation to the value of $\sigma = 2.927 \text{ \AA}$ obtained in ref. 13). Comparison of hydrogen-ammonia diffusion coefficients at 1 atmosphere is shown at the left.

Hydrogen-ammonia diffusion coefficients, cm^2/sec			
Temperature, $^\circ\text{C}$	Hydrogen mole fraction		
	0 (a)	0 to 1 (b)	1 (a)
25	0.7906	0.7830	0.7825
55	.9420	.9426	.9324
85	1.1038	1.0933	1.0926
$f_D^{(2)}(55)$	1.01036	-----	1.00006

^aCalculated.

^bExperimental.

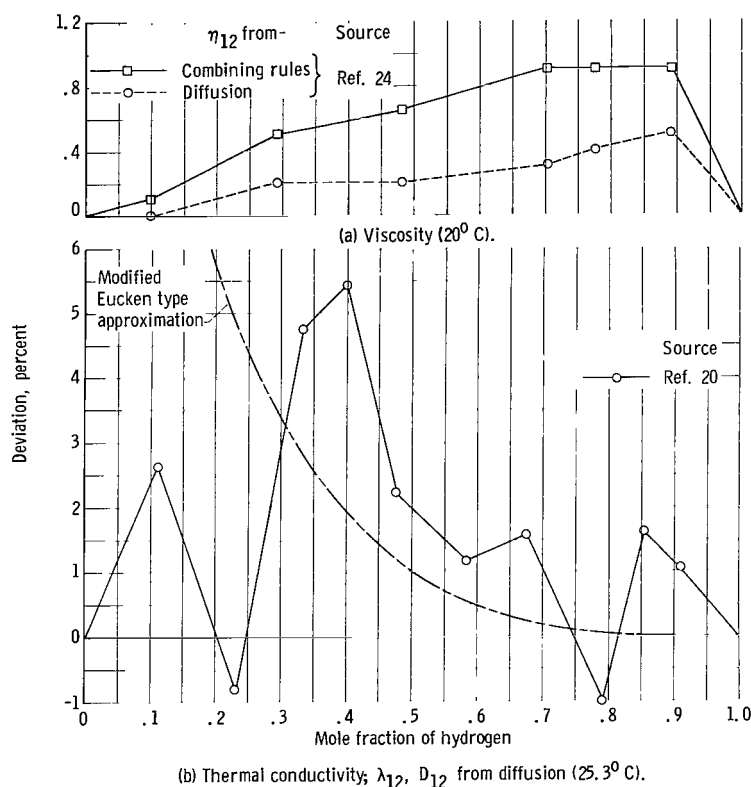


Figure 8. - Deviation of experiment from theory for hydrogen-ammonia mixtures.

The correction factor $f_D^{(2)}$ calculated at 55° C was applied at all three temperatures.

Viscosities and thermal conductivities for hydrogen-ammonia have been analyzed by assuming viscosity cross sections to fit exactly the viscosities of pure hydrogen and pure ammonia. Parameters characterizing the unlike interaction were taken from the combining rules of reference 2 (p. 600, $\sigma = 3.022$ and $\epsilon/k = 123^\circ \text{K}$) and also from diffusion ($\sigma = 2.931$, $\epsilon/k = 142.7^\circ \text{K}$; the value of σ from diffusion has been corrected according to eq. (8) with $f^{(3)} = 1.0015$). Experimental

viscosities of reference 24 are compared with theory in figure 8. The agreement is seen to be very good, with the diffusion force constants somewhat to

be preferred. Thus, it appears that the rigorous Chapman-Enskog theory for monatomic gases is quite acceptable even for mixtures involving polar gases.

Thermal conductivities were calculated from equations (3) and (6) with the resonant correction of reference 1 and by assuming $Z_{\text{NH}_3} = 2.11$ to fit the experimental value of reference 20 for pure ammonia at 25.3° C. A theoretical upper limit to the thermal conductivities was calculated by assuming $Z_{\text{NH}_3\text{-H}_2} = \infty$. Calculations are compared with experiment in figure 8. Also shown in this figure is the modified Eucken type approximation corresponding to $Z_{\text{NH}_3} = \infty$. In this case the correction for inelastic collisions is quite large and amounts to about 15 percent for pure ammonia. It does not seem possible to draw any firm conclusions concerning the theory from figure 8. The deviations are certainly larger than expected but show a large random, rather than systematic, fluctuation. The agreement is about as good as that for the hydrogen-nitrogen system (fig. 5).

CONCLUSIONS

Experimental transport properties of five selected binary systems have been investigated in terms of the best theoretical formulations presently available. This analysis leads to the following tentative conclusions with

regard to theory:

1. The diffusion coefficients and viscosities of gas mixtures, including mixtures with polyatomic and polar molecules, can be very well described in terms of the Chapman-Enskog theory, despite the fact that this theory is strictly rigorous only for monatomic gases.

2. There is no reason to doubt the validity of the Chapman-Enskog theory for the thermal conductivity of mixtures of monatomic gases; however, none of the experimental data are good enough to provide a really definitive test of the theory.

3. There are approximate methods that take account of the effects of internal energy on the heat conductivity of mixtures involving polyatomic and polar gases. These formulations seem promising, but again, experimental precision is too low to permit a meaningful evaluation of these methods.

And with regard to experimental data the following conclusions can be drawn:

1. There is already a large amount of mixture data of modest accuracy and precision (i.e., errors larger than 1 to 2 percent). Further experimentation of this sort will do little to further testing and understanding of theory.

2. The very best determinations of diffusion coefficients and mixture viscosities seem good enough to provide really meaningful tests of theory, including the second Chapman-Enskog approximation for diffusion and perhaps viscosity as well. More data of this quality would be most welcome.

3. There is an urgent need for thermal conductivity data of high accuracy and precision - little or none exists. It is proposed that such data may be acquired from precise measurements relative to the noble gases. Accurate conductivities for the monatomic gases can be computed from the best viscosity measurements by means of rigorous kinetic theory.

Lewis Research Center

National Aeronautics and Space Administration
Cleveland, Ohio, September 17, 1964

REFERENCES

1. Mason, E. A., and Monchick, L.: Heat Conductivity of Polyatomic and Polar Gases. Jour. Chem. Phys., vol. 36, no. 6, Mar. 15, 1962, pp. 1622-1639.
2. Hirschfelder, Joseph O., Curtiss, Charles F., and Bird, R. Byron: Molecular Theory of Gases and Liquids. John Wiley & Sons, Inc., 1954.
3. Mason, Edward A.: Forces Between Unlike Molecules and the Properties of Gaseous Mixtures. Jour. Chem. Phys., vol. 23, no. 1, Jan. 1955, pp. 49-56.

4. Muckenfuss, Charles, and Curtiss, C. F.: Thermal Conductivity of Multi-component Gas Mixtures. Jour. Chem. Phys., vol. 29, no. 6, Dec. 1958, pp. 1273-1277.
5. Hirschfelder, J. O.: Generalization of the Eucken Approximation for the Heat Conductivity of Polyatomic or Chemically Reacting Gas Mixtures. Proc. of Joint Conf. on Thermodynamic and Transport Properties of Fluids, 1957, pub. by Inst. Mech. Eng. (London), 1958, pp. 133-141.
6. Brokaw, Richard S.: Approximate Formulas for the Viscosity and Thermal Conductivity of Gas Mixtures. Jour. Chem. Phys., vol. 29, no. 2, Aug. 1958, pp. 391-397.
7. Walker, R. E., and Westenberg, A. A.: Molecular Diffusion Studies in Gases at High Temperature. III. Results and Interpretation of the He-Ar System. Jour. Chem. Phys., vol. 31, no. 2, Aug. 1959, pp. 519-522.
8. Iwasaki, H., and Kestin, J.: The Viscosity of Argon-Helium Mixtures. Tech. Rep. BRN-4-P, Brown Univ., Apr. 1963.
9. Thornton, E., and Baker, W. A. D.: Viscosity and Thermal Conductivity of Binary Gas Mixtures: Argon-Neon, Argon-Helium, and Neon-Helium. Proc. Phys. Soc. (London), vol. 80, Nov. 1962, pp. 1171-1175.
10. von Ubisch, Hans: Thermal Conductivities of Mixtures of Rare Gases at 29° and 520°. Arkiv Fysik, vol. 16, 1959, pp. 93-100.
11. Saxena, S. C.: Thermal Conductivity of Binary and Ternary Mixtures of Helium, Argon and Xenon. Indian Jour. Phys., vol. 31, 1957, pp. 597-606.
12. Wachsmuth, J.: Conduction of Heat in Mixtures of Argon and Helium. Zs. Physik, vol. 9, Apr. 1, 1908, pp. 235-240.
13. Bunde, Robert Edwin: Studies of the Diffusion Coefficients of Binary Gas Systems. Res. Lab. Rep. CM-850, Univ. Wisconsin, Aug. 8, 1955.
14. van Itterbeek, A., van Paemel, O., and van Lierde, J.: The Viscosity of Gas Mixtures. Physica, vol. 13, 1947, pp. 88-95.
15. Trautz, Max, and Binkelle, H. E.: Viscosity, Heat Conductivity and Diffusion in Gaseous Mixtures. VIII. The Viscosity of Hydrogen, Helium, Neon and Argon and Their Binary Mixtures. Ann. Physik, vol. 5, no. 5, 1930, pp. 561-580.
16. Barua, A. K.: Thermal Conductivity and Eucken-Type Factor for the Binary Mixtures H-He, H-Ne, H-Kr, and H-Xe. Indian Jour. Phys., vol. 34, 1960, pp. 169-183.
17. Madison, John J.: Analysis of Fixed and Condensable Gases by Two-Stage Gas Chromatography. Analytical Chem., vol. 30, no. 11, Nov. 1958, pp. 1859-1862.

18. Schmauch, L. J., and Dinerstein, R. A.: Response of Thermal-Conductivity Cells in Gas Chromatography. *Analytical Chem.*, vol. 32, no. 3, Mar. 1960, pp. 343-352.
19. Trautz, Max, and Baumann, P. B.: Viscosity, Heat Conductivity and Diffusion in Gas Mixtures. II. The Viscosities of Hydrogen, Nitrogen and Hydrogen-Carbon Monoxide Mixtures. *Ann. Physik*, vol. 5, no. 2, 1929, pp. 733-736.
20. Gray, P., and Wright, P. G.: The Thermal Conductivity of Mixtures of Nitrogen, Ammonia and Hydrogen. *Proc. Roy. Soc. (London)*, ser. A, vol. 263, no. 1313, Sept. 5, 1961, pp. 161-188.
21. Srivastava, B. N., and Srivastava, I. B.: Studies on Mutual Diffusion of Polar-Nonpolar Gas Mixtures. *Jour. Chem. Phys.*, vol. 36, no. 10, May 15, 1962, pp. 2616-2620.
22. Iwasaki, H., Kestin, J., and Nagashima, A.: The Viscosity of Argon-Ammonia Mixtures. *Tech. Rep. BRN-6-P*, Brown Univ., June 1963.
23. Baker, Charles E., and Brokaw, Richard S.: Thermal Conductivities of Gaseous H_2O , D_2O , and the Equimolar H_2O - D_2O Mixture. *Jour. Chem. Phys.*, vol. 40, 1964, pp. 1523-1528.
24. Trautz, Max, and Heberling, Robert: Viscosity, Heat Conductivity and Diffusion in Gas Mixtures. XVII. The Viscosity of Ammonia and Its Mixtures with Hydrogen, Nitrogen, Oxygen, and Ethylene. *Ann. Physik*, vol. 10, 1931, pp. 155-177.

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